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Electrolytic Behavior of Arsenic

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THE ELECTROLYTIC BEHAVIOR OF ARSENIC

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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DETERMINATION OF THE ELECTROLYTIC POTENTIAL

The electrolytic potential of arsenic, or the potential between an arsenic electrode and a solution normal with respect to arsenious ions, has never been accurately determined because of the difficulty of determining the arsenious ion concentration. In aqueous solution arsenious salts are strongly hydrolyzed and the metal ion concentration cannot be determined by conductivity measurements because of the presence of the acid which is formed by the hydrolysis. The conductivity of arsenious trichloride and hydrochloric acid solutions were measured by Zawidzki (Ber. d. D. Chem. Ges. 36, 1434, 1903) with results as shown in the following table in which V is the number of liters containing one mol and λ the equivalent conductivity.

V	λ $HCl+As(CH)_3$	λ' HCl	$\lambda' - \lambda$
16	366.3	368.5	+2.2
32	374.2	375.3	+1.0
64	379.6	379.2	-0.6

These results show clearly why conductivity measurements do not help in the determination of arsenious ion concentration. The ability of arsenious chloride to form arsenious cations has however been demonstrated by Kahlenberg and Lincoln (Jour. of Phys. Chem. 3, 28, 1899.) by measuring the conductivity of solutions of arsenious chloride in ethyl acetoacetate and nitrobenzene.

The potential between an arsenic electrode and a normal solution of arsenious chloride was measured by B. Neumann (Z. phys. Chem. 14, 220, 1894) and found to be 0.550 volts. From this value

it has been estimated by Abegg that the electrolytic potential of arsenic is +0.27 volts. using the scale in which hydrogen is zero and potassium negative, From the same figures Wilsmore (Z. phys. Chem. 35, 318, 1900) estimates that the electrolytic potential is "less than -0.293 volts", taking potassium as positive.

In order to obviate the difficulty of finding the arsenious ion concentration it was decided to employ the method used by Roderburg for tungsten and also by Rideal for uranium. For the measurement of the electrolytic potential of uranium Rideal used a solution of uranium tetrachloride in ethyl alcohol, The salt is not rapidly hydrolyzed in cold solution and the metal ion concentration can be determined by conductivity measurements. The relation between the electrolytic potential in aqueous and alcoholic solution is expressed by the following equation:

$$EP_w - EP_a = \frac{RT}{nF} \log \frac{P_w}{P_a}$$

in which EP_w and EP_a are the electrolytic potentials in water and alcohol respectively, and P_w and P_a the solution pressures of the metal in each solution. According to Carrara and Agostini (Z. Elektro-Chem. 11, 385, 1905) the value for the fraction $\frac{P_w}{P_a}$ is the same for all metals and for copper and cadmium $EP_w - EP_a$ = 0.11 volts. According to Roderburg the value for copper is 0.071 volts and this value is also used by Rideal.

In the work described below dry arsenious chloride was dissolved in dry alcohol and the potential between this and an

arsenic electrode was measured. The degree of ionization of the salt was determined by conductivity measurements and the electrolytic potential calculated by means of the Nernst equation.

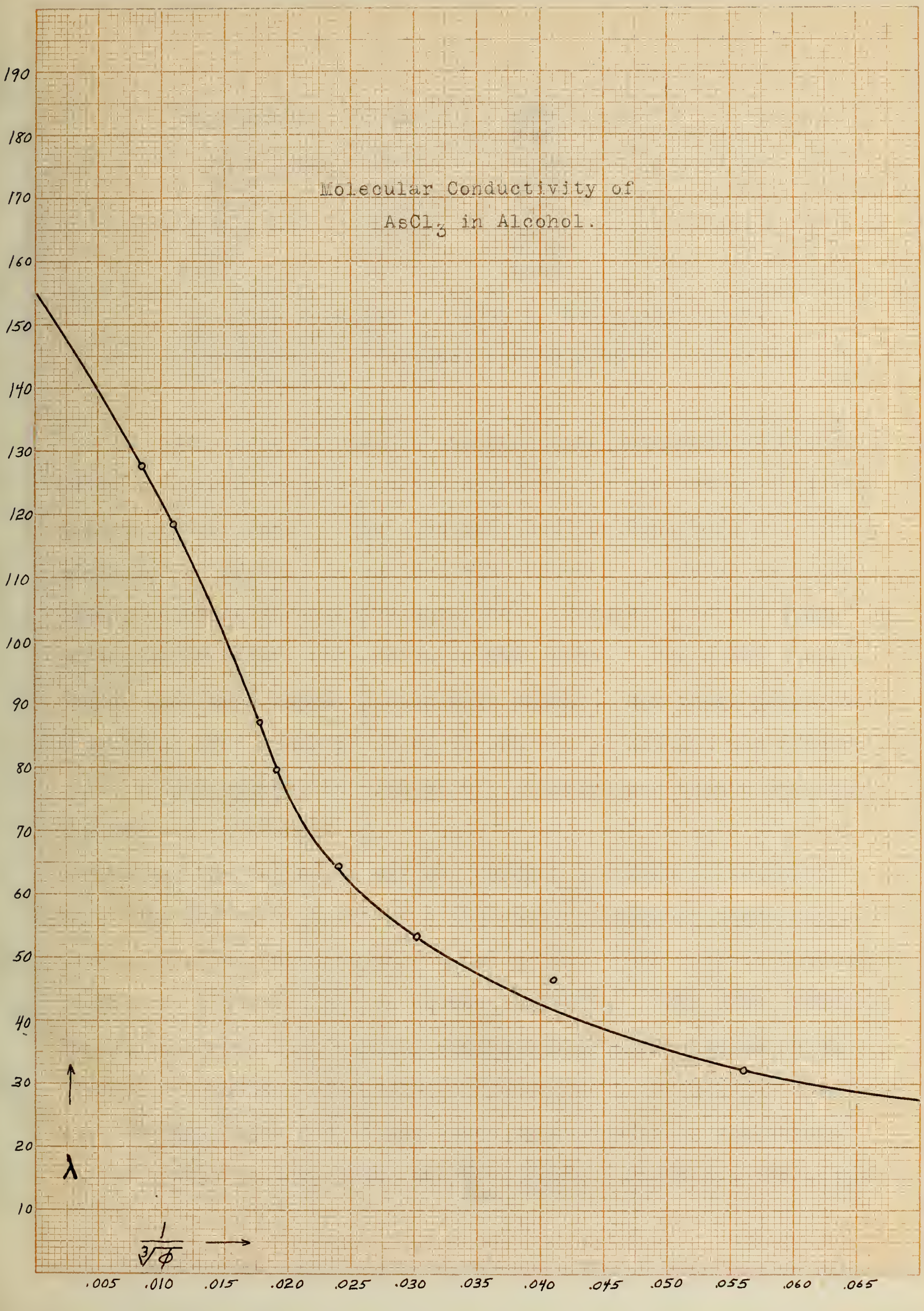
In taking up this work the first thing to be determined was whether or not arsenious chloride is hydrolyzed by cold absolute alcohol. If such hydrolysis does take place, then it is clear that during the process the conductivity of the solution will gradually increase on account of the hydrochloric acid which is formed. The conductivity of a solution containing .0807 grams of $AsCl_3$ in 50 cc. alcohol was measured at different time intervals with results as shown in the following table. The temperature was 20°.

Time. (After making solution).	Resistance
1 min.	74.3 ohms
2	74.6
3	74.9
4	75.5
6	76.2
9	76.9
14	77.3
24	77.5
54	77.7

It will be seen from this table that the resistance instead of being decreased, as might be expected was slightly increased. This is explained by the fact that arsenious chloride forms an addition product with alcohol (Walden-Z. phys. Chem. 43, 435). These results show that the change in arsenious ion concentration is slight and the solution quickly comes to equilibrium. The type of conductivity cell used permitted the exclusion of

air so that no moisture was taken up by the solution during the experiment.

In order to determine the degree of ionization of arsenious chloride it was necessary to measure the conductivity of several solutions of increasing dilution so that the value of λ_∞ the molecular conductivity at infinite dilution, could be obtained by extrapolation. The degree of ionization , α, is then found by the relation $\alpha = \frac{\lambda}{\lambda_\infty}$ The conductivity measurements were made by the Kohlrausch method. The $AsCl_3$ used was prepared by heating 40 parts of As_2O_3 with 100 parts of sulphuric acid to 100° C. and adding small pieces of fused sodium chloride. The $AsCl_3$ was distilled off and redistilled from concentrated sulphuric acid in order to make sure that it was dry. The absolute alcohol used was redistilled over CaO. Its conductivity was 1.56×10^{-6}. The results are shown in the following table and in the curve are plotted according to the method suggested by Kohlrausch in which values of λ, the molecular conductivity, are plotted as ordinates and $\frac{1}{\sqrt[3]{\phi}}$ (ϕ = volume in cubic centimeters in which one mol is dissolved) as abscissae. Values for λ were calculated by the relation $\lambda = \frac{\chi}{\eta}$ in which $\chi = \frac{\text{cell constant}}{\text{resistance}}$ and $\eta = \frac{1}{\phi}$. The values of λ shown below were corrected for the conductivity of the alcohol and give the average of several sets of readings in which both arsenious chloride prepared as described above and that furnished by E.H. Sargent Co. were used. There was good agreement between the readings obtained from these two samples of arsenious chloride. The value for λ_∞ obtained by plotting the following results is 155.0.



Molecular Conductivity of $AsCl_3$ in Alcohol.

Resistance	λ	$\frac{1}{\sqrt[3]{\phi}}$
36.8 ohms	53.5	.0303
61.0	64.6	.0240
98.7	79.4	.0191
113.9	87.0	.0177
331.	118.3	.0110
606.	127.2	.0085

Original solution = 5.0340 g. $AsCl_3$ per liter.
Temperature = 21°.
Conductivity of alcohol = 1.56×10^{-6}.
Cell constant = .05477.

In order to measure the electrode potential of arsenic in an alcoholic solution it was necessary to prepare an alcoholic auxiliary electrode. The electrode used by Roderburg and Rideal consisted of mercury in contact with alcohol saturated with mercurous chloride and lithium chloride. According to Roderburg the potential of this electrode is +0.193 volts. The arsenic electrodes used were copper plated with arsenic. For their preparation a solution of 5 grams of As_2O_3 in 300 cc. of 33% HCl was electrolyzed with a current density of 0.15 amperes per square decimeter. The deposit of arsenic was smooth, bright, and in good physical condition. The following system: Hg/HgCl and LiCl in al./$AsCl_3$ in al./As had an E. M. F. of 0.153 volts, therefore the electrode potential of the arsenic was +0.040 volts. The potential between an arsenic electrode and an aqueous solution of the same arsenious ion concentration is found by adding 0.071 to this value which gives 0.111 volts. The solution contained 0.176 mols of arsenious chloride per liter and it was found by conductivity measurement that $\lambda = 32.0$. Therefore $\alpha = \frac{\lambda}{\lambda_\infty} = \frac{32.0}{155.0} = 0.206$ and the arsen-

ious ion concentration was 0.176 x 0.206 = 0.0363. By substitution in the Nernst formula,

$$e = e_o + \frac{RT}{nF} \log \frac{C}{C_o}$$

the value e_o = +0.138 volts is obtained. Therefore the electrolytic potential of arsenic is +0.138 volts, using the scale in which hydrogen in zero and potassium negative. The measurement was repeated with a different arsenic electrode and a solution which contained .0704 mols of arsenious chloride per liter. In this case λ was found to be 46.6 and α .301. The calculated value for e_o was the same in this case as in the first determination, namely +0.138 volts. Arsenic should therefore come between hydrogen and copper in the electromotive series.

DETERMINATION OF THE OVERVOLTAGE

The overvoltage of hydrogen on arsenic was determined by measuring the back electromotive force , or polarization, of a cell which consisted of a platinium anode, arsenic cathode made as described above, and normal sulphuric acid electrolyte. The area of each electrode was one square centimeter. A gradually increasing electromotive force was applied to these electrodes until a milammeter indicated that current was just beginning to flow thru the cell, showing that decomposition of the electrolyte had just begun. The polarization of the cell caused by this impressed electromotive force was measured and by means of an auxiliary calomel electrode the anode and cathode polarizations, or overvoltages, were determined separately. Measurements were made by both the open and closed circuit methods. In the former, the back electromotive force is measured while the circuit furnishing the applied electromotive force is open. It is necessary to make the readings very quickly because depolarization begins as soon as the circuit is broken. In the closed circuit method the arm on the auxiliary electrode vessel is drawn out at the end to a small tube which is bent up to a horizontal position, as shown in the diagram, Fig. 1. This is placed in such a position that it almost touches the cathode in order to eliminate the IR drop caused by the resistance of the electrolyte. With this arrangement the

potential between the cathode and the calomel electrode can be measured without breaking the main circuit. The value for the overvoltage of hydrogen on arsenic obtained by the open circuit method was 0.379 volts, while that by the closed circuit method was 0.478 volts.

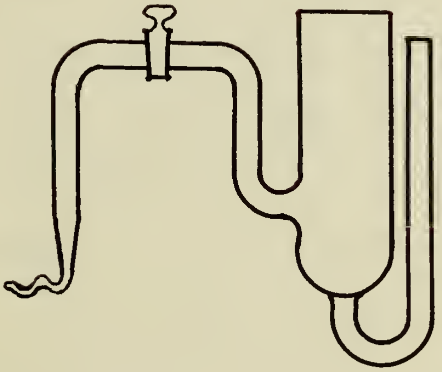


Fig. 1. Auxiliary Electrode Vessel.

THE ELECTROLYTIC DEPOSITION OF ARSENIC

The object of the work described below was to determine whether or not it would be possible to develope a method for the preparation of arsenic by electrolysis. The work done by previous investigators on the electrolytic deposition of arsenic has, almost without exception, had for its object the development of an analytical method for its quantitative determination. These have all been unsuccessful since the solutions which it is necessary to use for analytical purposes, namely solutions very dilute with respect to arsenious ions, are the most unfavorable for obtaining a good deposit. Theoretically arsenic should be deposited more easily than hydrogen, as indicated by its position in the electromotive series. It is true, however, of all metals and also of hydrogen that as the concentration of metal ions is increased, the voltage necessary for depositing the metal will be decreased, and conversely, as the concentration is decreased the necessary voltage is increased, in accordance with the Nernst formula. Therefore in solutions containing very few arsenious ions it is, in general, impossible to deposit the metal without simultaneous liberation of hydrogen which combines with the arsenic to form arsine gas and therefore causes a loss. The voltage necessary for the deposition of hydrogen can be raised by using solutions of alkalies but arsenic in alkaline solutions exists largely as arsenite or arsenate anions and only a small part is in cationic form. For

this reason alkaline solutions have not been used for analytical purposes. Another reason why dilute solutions are undesirable is that the formation of spongy, non-adherent deposits is favored. In many cases spongy deposits are obtained if dilute solutions are used but if the metal concentration is increased a good deposit is obtained.

In the past there has been very little work done on the electrolytic deposition of arsenic, Most investigators have worked on processes for determining arsenic as arsine formed by electrolytic hydrogen. Luckow (Z. analyt. Chem. 19, 14, 1880) states that the precipitation of arsenic from sulphide solutions is not complete. A. Classen and M. A. von Reis (Ber. d. D. Chem. Ges. 14, 1622, 1881) say that part of the arsenic in aqueous or oxalic acid solution will be reduced to metal and from hydrochloric acid solution all of the metal will be converted to arsine. The deposits obtained are not described and no detailed account of the work is given in either case. Neuman (Chem. Ztg. 30, 33, 1906) states that he succeeded in obtaining a quantitative deposit of arsenic from concentrated hydrochloric acid solution. He used a very small current in order to keep the voltage below the decomposition potential of hydrochloric acid (1.31 volts) and in this way prevented the liberation of hydrogen. It was necessary to use such a small current that seven days were required for the deposition of less than 0.5 grams of arsenic. He used a lead or silver anode for the purpose of removing the chlorine which was formed.

The method is of no practical importance because of the time required to complete the process but it shows that it is possible to obtain a good deposit of arsenic if the conditions are right. Patten and Mott (Trans. Am. Electrochem. Soc. 15, 261, 1909) obtained a good deposit of arsenic from a solution of $AsCl_3$ in acetone.

EXPERIMENTAL

The behavior of arsenic in the different solutions mentioned above and in several others was studied with results as described below. The electrolytic cell used consisted merely of a 400cc. beaker. The cathode was copper having an area of 33 sq. cm. and the anode was either platinium or carbon. The area of the platinium was 4 sq. cm. The carbon was obtained from an ordinary dry cell. In order to determine the efficiency of the process and to give an indication of the amount of arsine being formed, the electrolytic cell was connected in series with a copper coulometer. The theoretical weight of arsenic , deposited from $As^{\cdots}$ ions, which should be obtained by the current passed could be calculated from the weight of copper deposited, by making use of Farraday's Law, and the percentage yield was obtained by comparing the actual weight of arsenic with the theoretical.

TARTARIC ACID SOLUTIONS

Solutions were made by dissolving As_2O_3 in a concentrated solution of tartaric acid in water and electrolyzed with different current strengths as shown in the following table.

Anode	Wt. As_2O_3 dissolved in 250cc.	Amperes	Volts
Carbon	3 grams	.1	3.8
"	11 "	.2	3.0
"	11 "	.05	2.6
Platinum	11 "	.25	3.8

In every case the deposit was very spongy and non-adherent and the electrolyte contained a precipitate of finely divided particles of arsenic.

HYDROCHLORIC ACID SOLUTIONS

The deposits obtained from solutions of As_2O_3 in dilute hydrochloric acid were smooth, bright, firm, and had the appearance platinum. The results are tabulated below.

Wt. As_2O_3 in 300cc. Acid.	Strength of Acid.	Time of Electrolysis.	Wt. of Arsenic.	Yield Calc. as As...
5 grams	10%	10 hours	.324 grams	59%
5 "	20%	13 "	.406 "	62%
5 "	33%	17 "	.598 "	66%
5 "	50%	11 "	.518 "	61%
5 "	66%	8 "	.154 "	63%
5 "	33%	4 "	.139 "	82%
2.5 "	33%	6 "	.228 "	40%
2.5 "	50%	17 "	Deposit non-adherent.	
7.5 "	33%	Salt deposited on cathode.		
10 "	66%	17 hours	.523 grams	58%

These experiments were all run at room temperature as it was found that if the solutions were heated to 60° the deposit became blistered and cracked. The current density, with one or two exceptions was .15 ampere per square decimeter, The effect of varying the current density was determined by running in series four cells having different size cathodes. Results are shown in the following table.

Area of Cathode.	Current Density per sq. dec.	Wt. As.	Yield Calc. as $As^{\cdots}$
33 sq.cm.	.15 amperes	.192 g.	90%
20 "	.25 "	.111 g.	52%
10 "	.50 "	.056 g.	28%
4 "	1.25 "	.016 g.	7%

It will be seen from the first table that the best yield was obtained from a solution of 5 grams of As_2O_3 in 300cc. of 33% HCl and also that the yield was much higher if the electrolysis was for a short time than if it was continued for a long time. This falling off of efficiency is probably due to the chlorine which is formed at the anode and the oxidation of the arsenic to the pentavalent condition. (Neuman, Chem. Ztg. 30, 33. 1906). In every case the voltage gradually increased from about 1.8 volts at the beginning of the run to 3.0 volts at the end. This is due partly to the polarization caused by the bubbles of hydrogen on the cathode and probably also to the oxidation referred to above.

HYDROFLUOSILICIC ACID SOLUTIONS

Deposits obtained from this solution had the same appearance as those obtained from hydrochloric acid. The different strength solutions used are indicated below.

Wt. As_2O_3 in 300 cc. Acid.	Strength of Acid.	Time	Current Density.	Wt. of Arsenic.	Yield Calc. as As...
10 grams	50%	5hrs.	.15 am.	Deposit non-adherent.	
10 "	25%	23 "	.06 "	.175 g.	40%
Same solution		10 "	.06 "	.048 g.	26%
4 grams	25%	10 "	.06 "	.072 g.	39%
5 "	10%	10 "	.06 "	.159 g.	89%

These results show that the best solution is 5 grams of As_2O_3 dissolved in 300 cc. of 10% acid and that the efficiency drops off as the length of time increases in the same way as HCl solutions. It is necessary to use a lower current density in order to obtain a good deposit from this electrolyte than from HCl solutions. If the current density is too high, a precipitate of finely divided arsenic will form in the solution.

OXALIC ACID AND AMMONIUM OXALATE SOLUTIONS

Deposits of arsenic were obtained from solutions of As_2O_3 in concentrated oxalic acid and in ammonium oxalate solutions. These experiments were conducted at 65° C. using a current density of .12 amperes. The deposits were firm and adherent but were not smooth and bright. They seemed to contain occlusions of organic matter. For this reason and because oxalic

acid is rapidly decomposed by the current into CO_2, no quantitative data were obtained.

SODIUM SULPHIDE SOLUTIONS

In this case arsenic disulphide was used as solute instead of arsenious acid. The As_2S_2 is soluble in sodium sulphide solutions but upon standing for a short time or upon heating, the arsenic begins to precipitate out, probably in the form of sodium thioarsenite. Several different solutions were used for electrolytes but there was only one good deposit obtained and this result could not be duplicated. It is undoubtedly necessary, in order to obtain a good deposit, to use a solution in which no precipitate would be formed. A solution of sodium or ammonium polysulphide would probably fulfill these conditions but this was not determined experimentally. Details of the experiments are given in the following table.

Wt. As_2S_2 in 300 cc. sol.	Wt. Na_2S.	Temp.	Current Density.	Anode.	Remarks.
5 g.	25 g.	25°	.06 am.	Pt	Sulphide on anode.
Same solution		65°	.15 "	Pt	" " "
" "	+ 28 g. Na_2S	25°	.15 "	C	Good deposit.
3 g.	50 g.	19°	.09 "	C	Non-adherent.
3 g. + 10 g. KCN	50 g.	19°	.09 "	Pt	" "
8 g.	50 g.	24°	.09 "	C	" "
8 g. + 10 g. KCN	50 g.	24°	.09 "	Pt	" "

POTASSIUM CYANIDE SOLUTIONS

The deposits obtained from KCN electrolytes were very similar to those obtained from hydrochloric acid. It was necessary to use a lower current density because of the fact, as explained above, that in alkaline solutions only a small percentage of the arsenic exists in cationic form. For this reason it was also necessary to keep the total concentration of arsenic as high as possible in order to furnish the necessary number of arsenious cations. In these electrolytes there was no hydrogen evolved and the voltage remained constant through-out each run at from 2.5 to 3.0 volts depending on the solution and the temperature. Results are given below.

Wt. As_2O_3 in 300cc. sol.	Wt. KCN	Time	Current density	Temp.	Yield Calc. as $As^{\cdots}$
2.5 g.	8 g.	5 hrs.	.15 am.	23°	Non-adherent.
Same solution		15 "	.06 "	24°	" "
" "		6 "	.06 "	65°	" "
10 g.	10 g.	6 "	.12 "	24°	" "
10 g.	30 g.	24 "	.09 "	24°	83%
Same solution		22 "	.06 "	25°	94%
10 g.	20 g.	22 "	.06 "	25°	96%
Same solution		5 "	.12 "	65°	78%

CONCLUSIONS

Good deposits of arsenic were obtained from hydrochloric acid, hydrofluosilicic acid, and potassium cyanide solutions. The efficiency of the acid electrolytes was lower than the potassium cyanide. This is due to the liberation of hydrogen and formation of arsine in the former case. The potassium cyanide is also superior to the other electrolytes in that the efficiency does not decrease with the time. This work has been essentially a preliminary survey of the field. Results indicate that it should be possible to develope a satisfactory method for preparing arsenic by electrolysis of the cyanide solution.

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